

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the fuel cell which has a fuel electrode, an electrolyte layer, and an oxidizer agent electrode especially the fuel cell which can bring a highly efficient property to an oxidizer electrode, and its manufacture approach.

[0002]

[Description of the Prior Art] A fuel cell is a generator which generates electricity by supplying the porous electrode with which hydrogen content gas or organic alcohol, and the gas containing oxygen were given to the catalyst. Hydrogen oxidizes on an electrode, and a hydrogen ion conducts an electrolyte and moves to a cathode side. In a cathode, the supplied oxygen and the hydrogen ion which has moved react and water is generated. Moreover, an electron generates electrical energy by circulating an external circuit.

[0003] the on-site the object for space since the solid-state macromolecule form fuel cell using the solid-state poly membrane which has a hydrogen ion conductor as an electrolyte among fuel cells is compact, and high power density is obtained and it can operate by the simple system, and for stationing — it is observed as power sources for migration business, for cars, etc. That is, this fuel cell constitutes the unit cell by a fuel electrode, an oxidizer electrode, and the electrolyte membrane that consists of a poly membrane pinched by these constituting a generation-of-electrical-energy component, and forming the gas separator which forms fuel passage and oxidizer passage in the lateral surface of this generation-of-electrical-energy component, respectively. As polyelectrolyte film, the perfluorocarbon-sulfonic-acid film (for example, the Nafion trade name, Du Pont make) etc. is used.

[0004] This poly membrane is about 50–100 micrometers in thickness, where moisture is included, it shows hydrogen ion conductivity, but if it dries, will become an insulator and will not achieve an electrolytic function. Although hydrogen is circulated to the one side of this poly membrane and generated electricity by circulating air and oxygen to another side in a solid-state macromolecule form fuel cell, hydrogen and oxygen have the property (crossover phenomenon) which penetrates a macromolecule electrolyte membrane. It is known for the damp or wet condition as which especially a poly membrane functions that the amount of transparency of hydrogen will size-come to come, and this will cause consumption of hydrogen and the sharp property fall of a cell.

[0005] Various techniques are conventionally proposed to this gas crossover (for example, JP, 7-90111, A etc.). It sets on these techniques, and water is dispersedly mixing platinum and an oxide and generated at the reaction of hydrogen and oxygen within the film in a poly membrane, and the method of reducing membranous humidification and the crossover of gas etc. is indicated.

However, by the conventional approach, in order that a reaction may progress in the film, membranous micro destruction and thermofusion happen to the generation of heat, and it is not a desirable configuration from a viewpoint of the reinforcement of a cell. Moreover, diffusion of oxygen has problems, like since it is late compared with hydrogen, there is the need of diffusion of the oxygen within the film becoming rate-limiting, and being unable to perform a deployment of a precious metal catalyst, and mixing a precious metal catalyst into the film so much.

[0006]

[Problem(s) to be Solved by the Invention] As mentioned above, in the conventional technique, there is a problem which should solve versatility from the viewpoint of the reinforcement of a cell or a viewpoint of a deployment of a precious metal catalyst.

[0007] This invention was made in view of such a situation, and aims at offering the fuel cell which can aim at improvement in a property by prevention of the degradation by the transparency by the side of the oxidizer of liquid fuel, such as hydrogen and a methanol, simplification of a configuration, the amount-used reduction of noble metals, etc. especially by amelioration of an oxidizer electrode.

[0008] Moreover, this invention aims at offering the manufacture approach of a fuel cell that the cell engine performance and the product progression in quality can be planned especially paying attention to an oxidizer electrode.

[0009]

[Means for Solving the Problem] In order to attain the aforementioned purpose, in invention concerning claim 1 By a fuel electrode, an oxidizer electrode, and the electrolyte membrane that consists of a poly membrane pinched by these constituting a generation-of-electrical-energy component, and forming the gas separator which forms fuel passage and oxidizer passage in the lateral surface of this generation-of-electrical-energy component, respectively In the fuel cell which constitutes a unit cell said oxidizer electrode An oxide, At least one kind of metal chosen from platinum, palladium, a rhodium, and iridium Carbon powder or the catalyst of carbon fiber made [either] to carry out support distribution at least, The fuel cell characterized by including the catalyst, oxide, and polyelectrolyte thin layer which consists of solid-state polyelectrolyte material is offered.

[0010] In invention concerning claim 2, the fuel cell characterized by being the mixture with which the oxide of a catalyst, oxide, and a polyelectrolyte thin layer contains at least one kind of oxide chosen from a zirconia, the tin oxide, a titania, and Seria or these at least one oxide is offered in a fuel cell according to claim 1.

[0011] In invention concerning claim 3, the fuel cell characterized by the oxide of a catalyst, an oxide, and a polyelectrolyte thin layer being an oxide which was chosen from the SO₃H set, the COOH radical, the PO₃H set, and the OH radical, which has any one at least, and by which surface treatment was carried out is offered in a fuel cell according to claim 1 or 2.

[0012] In invention concerning claim 4, either to claims 1-3 is provided with the fuel cell characterized by forming a metal catalyst bed or a carbon layer between the gas separators which form a catalyst, an oxide and a polyelectrolyte thin layer, and oxidizing agent passage in the fuel cell of a publication.

[0013] In invention concerning claim 5, the fuel cell with which the amount of a metal catalyst bed is characterized by being in the range of 0.2 - 4 mg/cm² is offered in a fuel cell according to claim 4.

[0014] In this invention, a predetermined function is not obtained with less than two 0.2 mg/cm having made 0.2-4mg /of amounts of a metal catalyst bed (b) the range of 2 cm, but the amount of a metal catalyst bed is because gas circulation is checked with 4mg[/cm] 2 super-***** conversely.

[0015] In invention concerning claim 6, either to claims 1-5 is provided with the fuel cell with which the content of the solid-state polyelectrolyte material of a catalyst, an oxide, and a polyelectrolyte thin layer is characterized by being 10% or more by weight concentration in the oxidizer electrode of a publication.

[0016] In this invention, the reason for having made concentration of solid-state polyelectrolyte material into 10wt(s)% is for securing the ion conductivity in a catalyst, an oxide, and a polyelectrolyte thin layer. That is, the amount of polyelectrolytes and the relation of ion conductivity are because the resistance by which the sag in 0.2 A/cm² is equivalent to 5mV or less is shown, when the content occupied to the catalyst, oxide, and polyelectrolyte thin layer of the amount of polyelectrolytes cannot demonstrate effectiveness by percentage by weight less than [10wt%] but carries out to more than 10wt%. In addition, since a gas passageway will be closed by generation water and a cell property will fall if the concentration of solid-state

polyelectrolyte material exceeds 80wt(s)%, considering as less than [it] is desirable.

[0017] In invention concerning claim 7, either to said claims 1–6 is provided with the fuel cell characterized by the thickness of a catalyst, an oxide, and a polyelectrolyte thin layer being 5–30 micrometers in the fuel cell of a publication.

[0018] In this invention, the reason for having made thickness of a catalyst, an oxide, and a polyelectrolyte thin layer (a) into the range of 5–30 micrometers is because circulation of air is checked, when a predetermined function is not obtained with the thickness of a catalyst, an oxide, and a polyelectrolyte thin layer (a) being less than 5 micrometers but it exceeds 30 micrometers conversely.

[0019] In invention concerning claim 8, it is the approach of manufacturing the fuel cell of a publication to either to claims 4–7, and the liquefied constituent of a catalyst, oxide, and a polyelectrolyte thin layer is directly applied to the front face of a metal catalyst bed or a carbon layer, an oxidizer electrode is formed, and the manufacture approach of the fuel cell characterized by uniting this with a fuel electrode and an electrolyte membrane is offered.

[0020] It is the approach of manufacture the fuel cell of a publication to either to claims 4–7 in invention concerning claim 9 , and the resin sheet which has detachability beforehand is make to apply and dry the liquefied constituent of a catalyst , an oxide , and a polyelectrolyte thin layer , thermocompression bonding is carry out to the front face of a metal catalyst bed or a carbon layer after desiccation , an oxidizer electrode is form , and the manufacture approach of the fuel cell characterize by unite this with a fuel electrode and an electrolyte membrane is offer .

[0021] In invention concerning claim 10, it is the approach of manufacturing the fuel cell of a publication to either to claims 4–7, and the catalyst, the oxide, and the polyelectrolyte thin layer are beforehand formed in the shape of a sheet, and the manufacture approach of the fuel cell which carries out thermocompression bonding to the shape of sandwiches on both sides of this sheet between a metal catalyst bed or a carbon layer, and an electrolyte membrane, and is characterized by uniting this with a fuel electrode is offered.

[0022]

[Embodiment of the Invention] Hereafter, the operation gestalt of the fuel cell concerning this invention and its manufacture approach is explained with reference to a drawing.

[0023] 1st operation gestalt (drawing 1 , drawing 2 , drawing 3) drawing 1 is the mimetic diagram of the cellular structure of the fuel cell in the 1st operation gestalt of this invention. As shown in drawing 1 , the cel of this operation gestalt constitutes the generation-of-electrical-energy component with the fuel electrode 2, the catalyst, oxide and the polyelectrolyte thin layer 4 as oxidizer electrode 4A, and the metal catalyst bed 5, and the electrolyte membrane 3 that consists of a poly membrane pinched by these. The gas separators 8 and 9 which form fuel passage and oxidizer passage, respectively, and the gaseous diffusion layers 1 and 6 which face fuel passage and oxidizer passage are formed in each lateral surface of the fuel electrode 2 as this generation-of-electrical-energy component, and oxidizer electrode 4A, and, thereby, the unit cell is constituted.

[0024] A catalyst, oxide, and the polyelectrolyte thin layer 4 were taken as the configuration which contains a fluorine system sulfonic acid macromolecule as a polyelectrolyte including the zirconia including the carbon particle which supported palladium as a catalyst as oxide. Moreover, the metal catalyst bed 5 shall contain platinum.

[0025] If it explains in full detail, an electrolyte membrane 3 will be a cation-exchange poly membrane (only henceforth a "poly membrane") which has a sulfonic acid group as an ion exchange group so that a hydrogen ion can be conducted, and a hydrogen ion will penetrate it alternatively in the direction of thickness. This is the sulfonic acid exchange film (for example, a trade name: the Nafion film, product made from Du Pond) of a fluorine system, and thickness is 50 micrometers.

[0026] An electrolyte membrane 3, oxidizer electrode 4A which consists of a metal catalyst bed 5, and a catalyst, an oxide and a polyelectrolyte thin layer 4, and the fuel electrode 2 are unified through the thermocompression bonding by the hotpress. The gaseous diffusion layers 1 and 6 are formed with porous porous carbon, and porosity is 70 – 95% of thing. In addition, the thing in which

the thin layer containing the carbon powder which has pore smaller than the pore diameter of porous carbon, and a fluororesin was formed on the front face of this porous carbon may be used for the gaseous diffusion layers 1 and 6. Moreover, porous carbon may also make a fluororesin contain, may be sintered and may use what gave water repellence.

[0027] The fuel electrode 2 was manufactured according to the following process. That is, the carbon paper (content 25wt% of polytetrafluoroethylene) given a water-repellent finish was prepared as a gaseous diffusion layer 1, and the catalyst paste was applied to this. the fluorine system sulfonic acid macromolecule resin liquid (what dissolved pitch 5wt% in the mixed solution of propanol and water) as the cation-exchange-resin solution 3, for example, an electrolyte membrane, with the catalyst paste same to the carbon particle which supported platinum 40wt% as a catalyst — in addition, it is made the shape of a paste. Only the amount from which platinum becomes 0.4 mg/cm² was applied, this paste was dried at 70 degrees C, and the solvent was removed.

[0028] Next, oxidizer electrode 4A was manufactured according to the following process like the case of the fuel electrode 2, and abbreviation. That is, the carbon paper (content 25wt% of polytetrafluoroethylene) given a water-repellent finish was prepared as a gaseous diffusion layer 6, and the catalyst paste was applied to this. the fluorine system sulfonic acid macromolecule resin liquid (what dissolved pitch 5wt% in the mixed solution of propanol and water) as the cation-exchange-resin solution 3, for example, an electrolyte membrane, with the catalyst paste same to the carbon particle which supported platinum 40wt% as a catalyst — in addition, it is made the shape of a paste. Only the amount from which platinum becomes 0.2 mg/cm² was applied, this paste was dried at 70 degrees C, and the solvent was removed.

[0029] Next, the manufacture approach of a catalyst, an oxide, and the polyelectrolyte thin layer 4 is described.

[0030] First, the method of manufacturing the paste for spreading is described. as a catalyst — palladium — 50wt(s)% — the supported carbon particle was used. Water was added and stirred to this, the impalpable powder (specific-surface-area 60m²/g) of a zirconia was added, the same fluorine system sulfonic acid macromolecule resin liquid as having used, when manufacturing the fuel electrode 2 further was added and stirred, and the paste for spreading was manufactured. As a weight ratio when drying, the mixed rate of a paste was mixed so that it might be set to palladium 50wt% support carbon:oxide:polyelectrolyte =50:30:20 (percentage by weight). Moreover, it adjusted suitably and water was used so that the viscosity of a paste might be suitable for spreading.

[0031] As an amount of palladium, the paste manufactured by the above-mentioned approach was applied to the front face of the metal catalyst bed 5 of oxidizing agent electrode 4A so that it might become 0.2 mg/cm², and it dried. In order to carry out smooth [of the front face] furthermore, the roll with which predetermined thickness was prescribed was passed.

[0032] Thus, thermocompression bonding of the oxidizer electrode 4A (the metal catalyst bed 5, and a catalyst, an oxide and a polyelectrolyte thin layer 4) was carried out to the fuel electrode 2 and electrolyte membrane 3 which were manufactured with the hotpress (130 degrees C, 80kg/cm²). Then, the separator with which slot shaping was carried out for reactant gas supply was made to equip, and the fuel cell was completed.

[0033] Thus, it generates electricity by humidifying and supplying fuel gas (or liquid fuel, such as a methanol) and air (or oxygen) to the completed fuel cell at temperature respectively lower 5–10 degrees C than the operating temperature of a cell.

[0034] Next, the performance evaluation of the fuel cell of this completed operation gestalt is explained.

[0035] As a fuel cell to contrast, the amount of platinum of oxidizer electrode 4A applied the conventional fuel cell which is 0.4 mg/cm². That is, as this conventional fuel cell, a catalyst, an oxide, and the polyelectrolyte thin layer 4 are excepted from the configuration of this operation gestalt, and the amount of platinum in the metal catalyst bed 5 is conversely made into 0.4 mg/cm². The manufacture process of this conventional fuel cell was manufactured according to the almost same process as this operation gestalt mentioned above.

[0036] Drawing 2 shows each current-voltage characteristic about the fuel cell (A) by this operation gestalt, the fuel cell (B) by the 2nd operation gestalt mentioned later, and the fuel cell (C) by the example of a comparison (about the property of the 2nd operation gestalt, it mentions later). In addition, the flow rate was adjusted and measured so that the actuation conditions of a cell were 70 degrees C in cell temperature, and a utilization factor with hydrogen and oxygen might become pure hydrogen as a fuel and they might become 70% and 40% about air as an oxidizer, respectively with each current density (however, two or less 100 mA/cm, 100mA/cm the same flow rate as 2).

[0037] As shown in drawing 2, in the fuel cell (A) by this operation gestalt, the electrical potential difference showed the high value also with each current density highly [open circuit voltage] compared with the fuel cell (C) by the example of a comparison. Since the catalyst was used for hydro-acid-izing from which open circuit voltage has crossed the catalyst by the side of an oxidizing agent in the fuel cell of the example of a comparison, the internal current flowed also in the state of off, for this reason polarization arose, and open circuit voltage became low as that result. On the other hand with the fuel cell by this operation gestalt, by existence of a catalyst, an oxide, and the polyelectrolyte thin layer 4 When the hydrogen which the trap of the hydrogen is carried out, and the oxygen from an oxidizing agent is adsorbing with the oxide further, and has crossed oxygen by existence of a precious metal catalyst further reacts, in order to generate water, Since reaction area also becomes large, without [therefore] being used for oxidation of hydrogen, polarization of a cell of the precious metal catalyst of oxidizer electrode 4A is also small, and it can show high open circuit voltage and the high electrical potential difference in each current density.

[0038] Moreover, although the amount of noble metals of the fuel cell by this operation gestalt and the fuel cell by the example of a comparison turned into the same amount per unit area of a cell, it became clear that an output is high, therefore the output per amount of platinum is large.

Furthermore, when the property was compared about the fuel cell of the conventional type which makes two or more [0.2mg //cm] the catalyst of the cathode which does not contain an oxide, fixes the amount of palladium contained in the layer containing an oxide, and has platinum of the same amount as this, all had the high property of this operation gestalt. In addition, when the cell as an example of a comparison which made the total amount of platinum the value exceeding 4 mg/cm² was created, it became the same as the property of the fuel cell of a conventional type, and a predominance in the cell of this example of a comparison was not able to be checked.

[0039] In order to check such hydrogen trap effectiveness, a hydrogen side is pressurized to 10kpa(s) and the result of having measured change of open circuit voltage is shown in drawing 3. Although open circuit voltage hardly changed with the fuel cell (A) by this operation gestalt even if the pressure of hydrogen became high as shown in this drawing 3, open circuit voltage fell greatly in the fuel cell (B) by the example of a comparison.

[0040] Since the hydrogen which the hydrogen pressure force became large by existence of a catalyst, an oxide, and the polyelectrolyte thin layer 4, this adsorbed hydrogen even if the amount of transparency of hydrogen increased, and has penetrated it since there is much supply of the adsorption oxygen by the oxide oxidizes smoothly, and becomes water, and a cathode catalyst is maintained in reaction area while it has been large, it is because open circuit voltage is also high and it is maintainable.

[0041] Moreover, in this operation gestalt, concentration of a polyelectrolyte was made into 20wt (s)% with the mixture after desiccation. as the percentage by weight occupied to a catalyst, an oxide, and the polyelectrolyte thin layer 4 when this amount of polyelectrolytes and the relation of ion conductivity are investigated, although this was for securing the ion conductivity in a catalyst, an oxide, and the polyelectrolyte thin layer 4 — more than 10wt% — when it existed, it turned out that the resistance in which the sag in 0.2 A/cm² is equivalent to 5mV or less is shown. Therefore, the electrolyte beyond 10wt% is required for a catalyst, an oxide, and the polyelectrolyte thin layer 4.

[0042] As mentioned above, in the fuel cell of this operation gestalt, the thin film which comes to contain the catalyst and polyelectrolyte material which carried out carbon powder support

distribution of oxide and the noble metals was formed in the front face containing the metal catalyst of oxidizing agent electrode 4A. By forming the thin layer of such a presentation in a platinum catalyst front face, the hydrogen which has penetrated the electrolyte membrane 3 sticks to noble metals, such as palladium, and an oxygen component sticks to an oxide among the air supplied to the cathode. And water is generated when this oxygen and hydrogen react on a precious metal catalyst. Therefore, it can prevent that hydrogen reaches the metal catalyst from which the reduction reaction of oxygen occurs, and checks the reduction reaction of oxygen, the catalyst area for oxygen reduction can be maintained in the large condition, for this reason, polarization of the cell in oxidizer electrode 4A can be kept small, and high performance-ization of a cell can be realized.

[0043] the 2nd operation gestalt (drawing 4 , drawing 5 , drawing 2) — the 2nd operation gestalt is explained below. The structure of the cell by the 2nd operation gestalt is shown in drawing 4 .

[0044] Drawing 4 is the mimetic diagram of the cellular structure of the fuel cell in the 2nd operation gestalt of this invention. As shown in drawing 4 , the cel of this operation gestalt constitutes the generation-of-electrical-energy component with the fuel electrode 2, the catalyst, the oxide and the polyelectrolyte thin layer 4 as oxidizing agent electrode 4A, and the carbon layer 7, and the electrolyte membrane 3 that consists of a poly membrane pinched by these. The gas separators 8 and 9 which form fuel passage and oxidizer passage, respectively, and the gaseous diffusion layers 1 and 6 which face fuel passage and oxidizer passage are formed in each lateral surface of the fuel electrode 2 as this generation-of-electrical-energy component, and oxidizer electrode 4A, and, thereby, the unit cell is constituted.

[0045] The carbon layer 7 is formed between the catalyst, the oxide and the polyelectrolyte thin layer 4, and the gas-passageway plate 9 that forms oxidizer passage. That is, with this 2nd operation gestalt, the metal catalyst bed 5 of oxidizer electrode 4A is lost, and the point which has formed the catalyst, the oxide, and the polyelectrolyte thin layer 4 in the front face of the gaseous diffusion layer 6 of oxidizer electrode 4A directly differs from the 1st operation gestalt.

[0046] With this operation gestalt, as it was the following, oxidizer electrode 4A was manufactured.

[0047] First, the mixture of the polytetrafluoroethylene of a porous carbon porous body (porosity 85%, thickness 90 micrometers) and carbon powder (specific-surface-area 240m²/g) was applied so that it might become the thickness of 30 micrometers. This was heat-treated in 20-minute air at 350 degrees C. Water repellence has been given by this heat treatment.

[0048] Furthermore, water was added to the carbon fiber (diameter of fiber 50nm) and titanium oxide (70m²/g) which supported platinum 40wt%, and viscosity accommodation was carried out, in addition, it stirred so that the sulfonic acid giant molecule of a 5wt(s)% fluorine system might be set to platinum 50wt% support carbon:oxide:polyelectrolyte =40:30:30 (percentage by weight) to a pan, and slurry liquid was obtained. This slurry liquid was applied on the polytetrafluoroethylene sheet, and it dried. Coverage was adjusted so that the thickness after desiccation might be set to 30 micrometers. It put on the porous carbon which prepared the thin film sheet of this polytetrafluoroethylene previously, the hotpress was carried out on 140 degrees C and 40kg/cm² conditions, and oxidizer electrode 4A was obtained. In addition, the amount of platinum of this electrode was 0.35 mg/cm². Thus, using the obtained oxidizer pole, the same fuel cell as the 1st operation gestalt was constituted, and the cell property was measured.

[0049] As mentioned above, that current-voltage characteristic is shown in drawing 2 with the fuel cell (C) according the property of the fuel cell (B) by this 2nd operation gestalt to the example of a comparison. The fuel cell by this operation gestalt showed the property better than the fuel cell by the example of a comparison so that clearly from this drawing 2 .

[0050] Although the catalyst bed of oxidizer electrode 4A itself performs oxidation reaction of hydrogen adsorption and oxygen supply, and the penetrated hydrogen with this operation gestalt, since oxidation reaction of the hydrogen which oxygen adsorption took place by the whole catalyst bed, and sufficient quantity of adsorption oxygen existed, therefore has been penetrated near the interface of a catalyst bed-poly membrane occurs, there is little effect of the catalyst effective-surface product on original oxygen reduction at a catalyst bed.

[0051] In order that water may generate on a front face in this way and this water may give moderate humidity to the macromolecule of oxidizer electrode 4A on the other hand, hygroscopic moisture is effectively given for the polyelectrolyte which exists in a catalyst. By this, the activity of an electrode can carry out long duration maintenance. As shown in drawing 5, cell voltage (0.2 A/cm²) was stable over the long period of time compared with the fuel cell by the example of a comparison in the fuel cell by this operation gestalt. This shows that the catalyst, the oxide, and the polyelectrolyte thin layer 4 are acting effectively over a long period of time, and it was admitted that property stability also improved by this.

[0052] In the fuel cell of the above 2nd operation gestalt 2, since the hydrogen which adsorption of oxygen became easy and have penetrate the electrolyte membrane 3 since the thin layer which come further to contain the catalyst and solid-state polyelectrolyte material which made carbon fiber carry out support distribution of the platinum be form in the front face of the air gas diffusion layer 6 including oxide can be oxidize on a precious metal catalyst, hydrogen react with oxygen easily and generate water. In this case, in order to be dependent on the concentration of the hydrogen which stuck to the water generation reaction since adsorption oxygen existed so much by existence of an oxide, it happens very near an electrolyte membrane 3 and the oxidizer electrode 4A. For this reason, most precious metal catalysts are applicable to the reduction reaction of oxygen. For this reason, an oxygen reduction reaction can advance smoothly, and polarization of oxygen reduction can be made small and can attain high performance-ization of a cell. Moreover, since effectiveness continues over a long period of time effectively [in order that the generated water may carry out humidity of the polyelectrolyte in a catalyst / a catalyst], a cell property stable for a long period of time is maintainable.

[0053] With other 1st and 2nd operation gestalten which carried out operation gestalt ****, as oxide of a catalyst, oxide, and the polyelectrolyte thin layer 4, although a zirconia or titanium oxide was applied, also when it replaced with these and the tin oxide or Seria was applied, the almost same result as said each operation gestalt was obtained.

[0054] Furthermore, the oxide which has SO₃H, COOH, PO₃H, and an OH radical for the front face of a zirconia, titanium oxide, or the tin oxide and by which surface treatment was carried out was applied as oxide of the polyelectrolyte thin layer 4. Namely, it was immersed in the solution of an oleum / concentrated-sulfuric-acid = 1/4, 100g (100m²/g) of impalpable powder of (1) zirconia (ZrO₂) was heat-treated at 90 degrees C for 1 hour, and the oxide was further heat-treated at 500 degrees C for 1 hour. When infrared analysis (FTIR) of the obtained powder was performed, existence of surface-SO₃H has been checked. (2) It was immersed in the alkali solution of 2 M/L, and heat-treated after desiccation (500 degrees C - 1 hour), the impalpable powder of titanium oxide was rinsed after that, it dried except for excessive alkalinity, and the titanium oxide powder which carried out surface preparation with the hydroxide (-OH) was obtained. (3) The tin-oxide impalpable powder which was immersed in condensed phosphoric acid (105% of phosphoric-acid concentration), dried after that, heat-treated the tin oxide (300 degrees C - 1 hour), rinsed it, and carried out surface treatment (-PO₃H) was obtained. The thin layer of a catalyst, an oxide, and a polyelectrolyte was formed using the oxide which carried out surface treatment as mentioned above.

[0055] By such surface treatment, the maintenance capacity (water adsorption capacity force per 1g of oxides) of water becomes high compared with an oxide without surface treatment, and the water holdout in a catalyst improves. This is effective in order to keep high the ion conductivity of the solid-state macromolecule which is needed for the reduction reaction of oxygen. The long-term stability of the fuel cell by these operation gestalten is based on the effectiveness using an oxide [finishing / surface treatment]. According to these operation gestalten, compared with the oxide with which surface treatment like the conventional example shown in drawing 5 is not carried out, a degradation rate becomes low. Especially in the oxide containing SO₃H set, the degradation rate turned into about 70% of the degradation rate of drawing 5, and it was checked that remarkable effectiveness is acquired.

[0056] Moreover, as for this invention, it is needless to say that it is not limited to the above operation gestalt and can carry out in various modes. For example, with said each operation

gestalt, although hydrogen was used as fuel gas, it is applicable also to oxidizer electrode 4A of the methanol supply mold fuel cell using the methanol solution of various concentration. At this time, the methanol penetrated instead of hydrogen is oxidized and reduction of the catalyst effective area of oxidizer electrode 4A can be prevented.

[0057] moreover, application of the rhodium and iridium which have hydro-acid-izing and oxygen reduction capacity although platinum and palladium were applied as a precious metal catalyst with said operation gestalt — the porphyrin complex compound (especially a cobalt metal is desirable) in a complex with a metal is also variously applicable.

[0058] Moreover, as oxide, what adds antimony etc. to the tin oxide or the tin oxide, and has electronic conductivity although the zirconia and the titania were applied, and the thing added [silicon oxide / Seria, / a magnesium oxide silicon oxide] in order to change surface basicity into a zirconia are also effective.

[0059] moreover, as a method of manufacturing a catalyst, an oxide, and the polyelectrolyte thin layer 4 Polytetrafluoroethylene and other thermoplastic organic substance polymers are added to such mixture as a binder. The manufacturing method which makes a fuel cell what unified what sandwiched what was fabricated on the sheet between the porous objects of carbon and poly membranes which applied the gaseous diffusion layer 6 metallurgy group catalyst, and put the fuel electrode 2 further with thermocompression bonding means, such as a hotpress, is also possible.

[0060] ** By forming the thin layer of such a presentation in a front face including a metal catalyst, the hydrogen which has penetrated the electrolyte membrane 3 sticks to noble metals, such as platinum, palladium, a rhodium, and iridium, and an oxygen component sticks to the oxide of SO₃H set, a COOH radical, PO₃H set, or an OH radical by which surface treatment was carried out so that any one might be included at least among the air supplied to the cathode. And water is generated by reacting on this oxygen, the penetrated hydrogen, and a precious metal catalyst. Therefore, it can prevent that hydrogen reaches the metal catalyst from which the reduction reaction of oxygen occurs, and checks the reduction reaction of oxygen, the catalyst area for oxygen reduction can be maintained in the large condition, and, for this reason, polarization of the cell in oxidizer electrode 4A can be kept small.

[0061] ** Since the precious metal catalyst which can oxidize the hydrogen which adsorption of oxygen became easy and has penetrated the electrolyte membrane 3 since the oxide or the oxide which carried out surface treatment is included on the front face of the gaseous diffusion layer 6 is included, hydrogen reacts with oxygen easily and generates water. In this case, in order to be dependent on the concentration of the hydrogen which sticks to a water generation reaction since adsorption oxygen exists so much by existence of an oxide, it happens very near an electrolyte membrane 3 and the oxidizer electrode 4A. For this reason, most precious metal catalysts are applicable to the reduction reaction of oxygen. For this reason, an oxygen reduction reaction can advance smoothly, and polarization of oxygen reduction can be made small and can attain high performance-ization of a cell.

[0062]

[Effect of the Invention] As explained above, according to the fuel cell concerning this invention, improvement in a property by prevention of the degradation by the transparency by the side of the oxidizer of liquid fuel, such as hydrogen and a methanol, simplification of a configuration, the amount-used reduction of noble metals, etc. can be aimed at especially by amelioration of an oxidizer electrode.

[0063] Moreover, according to the manufacture approach of the fuel cell concerning this invention, especially paying attention to an oxidizer electrode, the cell engine performance and the product progression in quality can be planned.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The block diagram showing the unit cell of the oxidizer electrode in the 1st operation gestalt 1 of this invention.

[Drawing 2] The graph which shows the property comparison with the fuel cell by the operation gestalt of this invention, and the fuel cell by the example of a comparison.

[Drawing 3] The graph which shows the effect comparison of the hydrogen pressure force of cell open circuit voltage for the 1st operation gestalt and the example of a comparison of this invention.

[Drawing 4] The block diagram showing the unit cell of the oxidizer electrode in the 2nd operation gestalt of this invention.

[Drawing 5] The graph which shows the long duration property comparison with the fuel cell by the 2nd operation gestalt of this invention, and the fuel cell by the example of a comparison.

[Description of Notations]

- 1 Gaseous Diffusion Layer
- 2 Fuel Electrode (Anode Catalyst Bed)
- 3 Electrolyte Membrane
- 4A Oxidizer electrode
- 4 Catalyst, Oxide, and Polyelectrolyte Thin Layer
- 5 Metal Catalyst Bed (Cathode Catalyst Bed)
- 6 Gaseous Diffusion Layer
- 7 Carbon Layer
- 8 Nine Gas separator

[Translation done.]